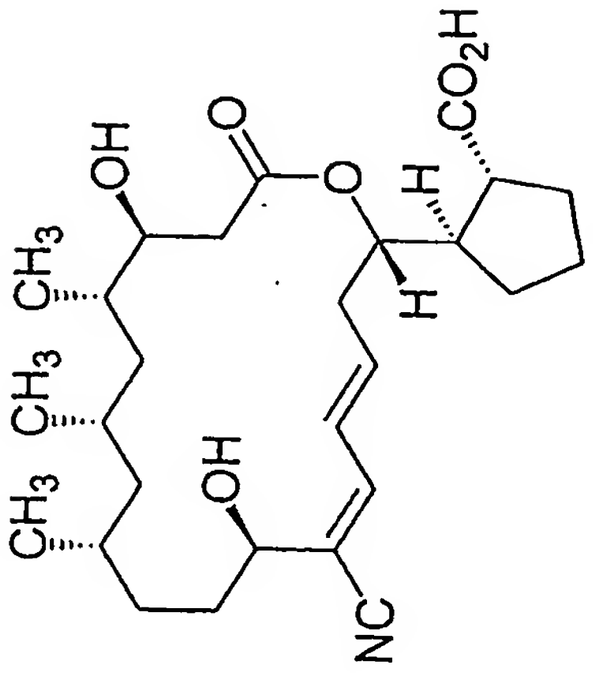
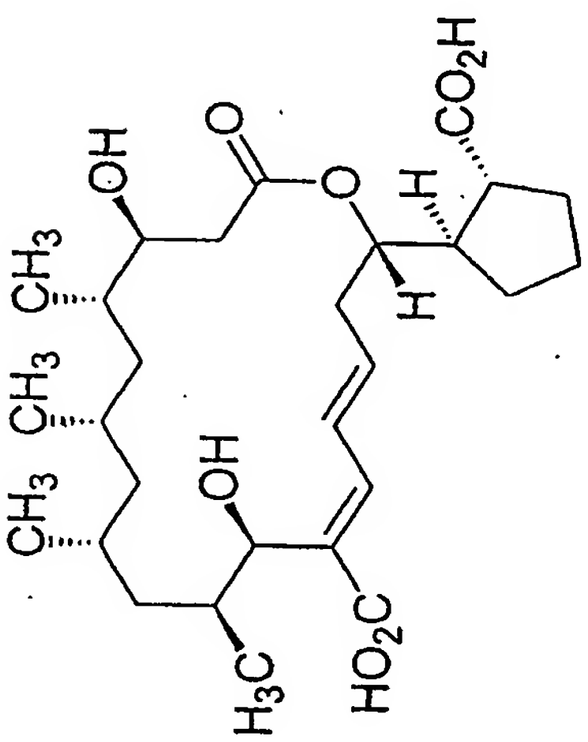
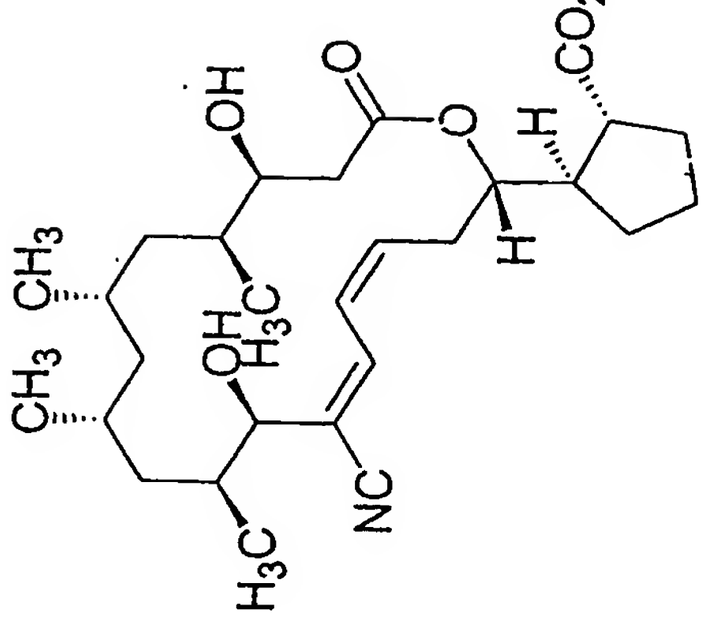


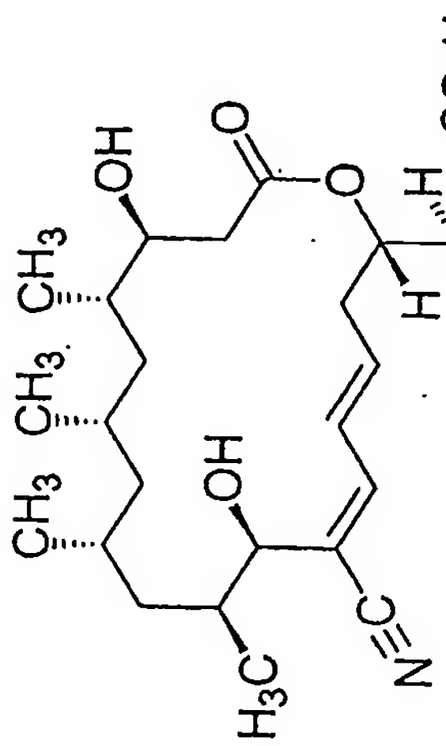
10-desmethyl borrelidin (3)



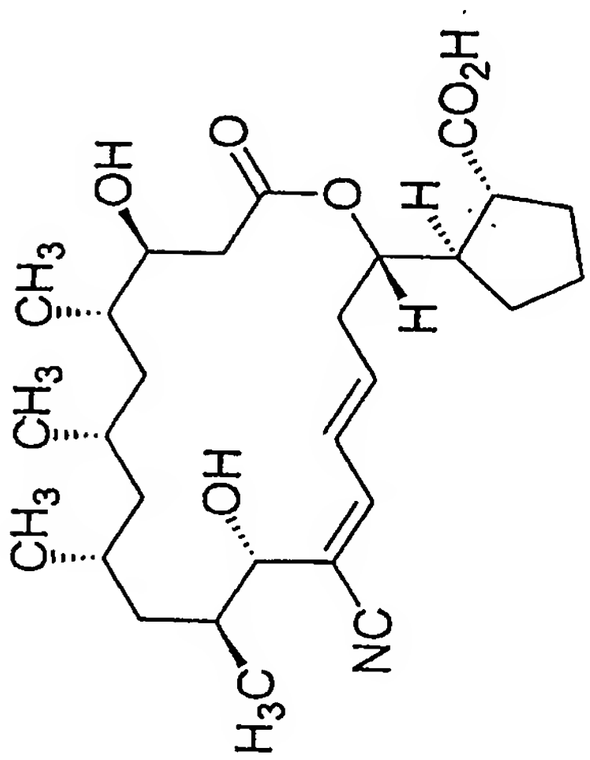
12-desnitrile-12-carboxyl borrelidin (2)



14,15-cis-borrelidin (5)



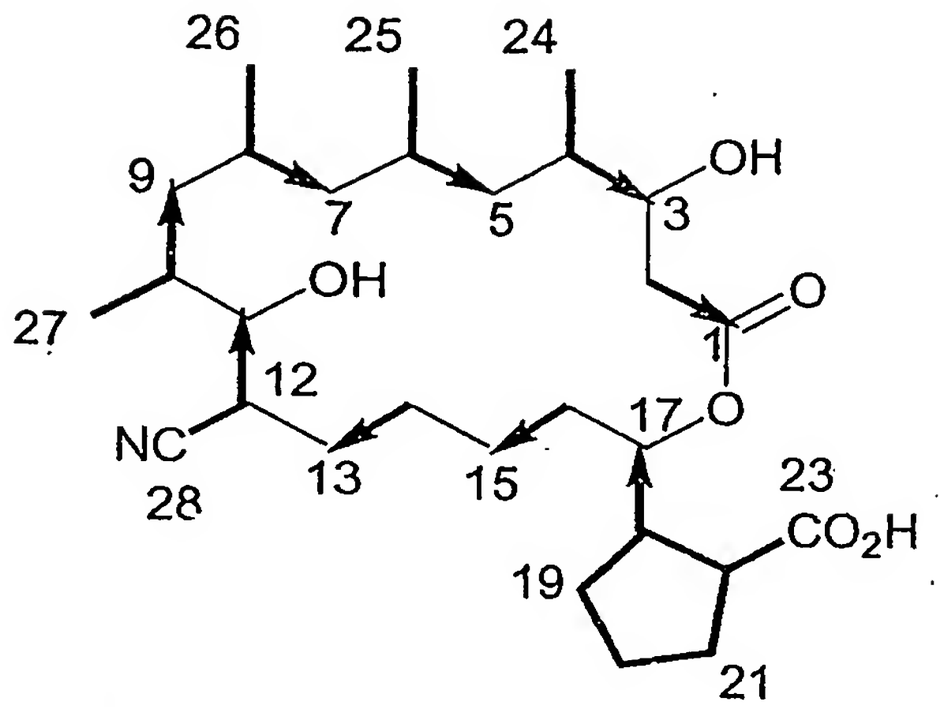
Borrelidin (1)



11-*epi* borrelidin (4)

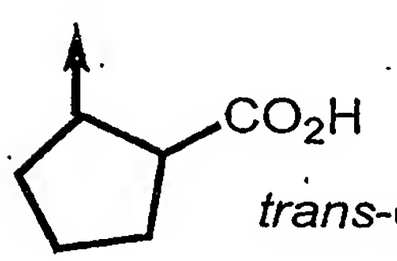
Figure 1

Figure 2



[1,2-^{13}C]sodium acetate

[2,3-^{13}C]sodium propionate



trans-cyclopentane-1,2-dicarboxylic acid

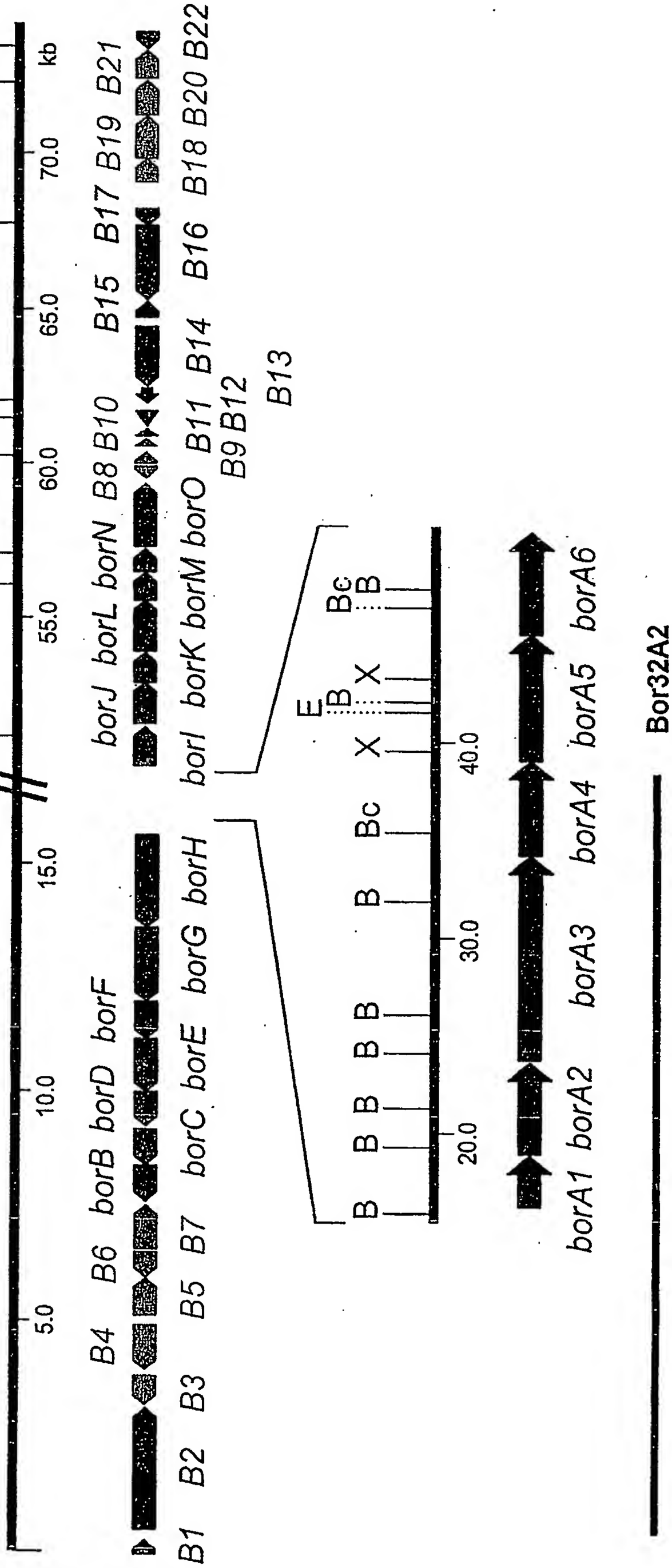

kb
70.0
65.0
60.0
55.0
15.0
10.0
5.0
40.0
30.0
20.0
B15 B17 B19 B21
B14 B16 B18 B20 B22
B12 B13
borJ borL borN B8 B10
borI borK borM borO B11
B9 B12
borE borG borH
borD borF
B4 B6 borB borD
B1 B2 B3 B5 B7 borC
borA4 borA5 borA6
borA3
borA2
borA1
Bor32A2
Bor19B9

Figure 3

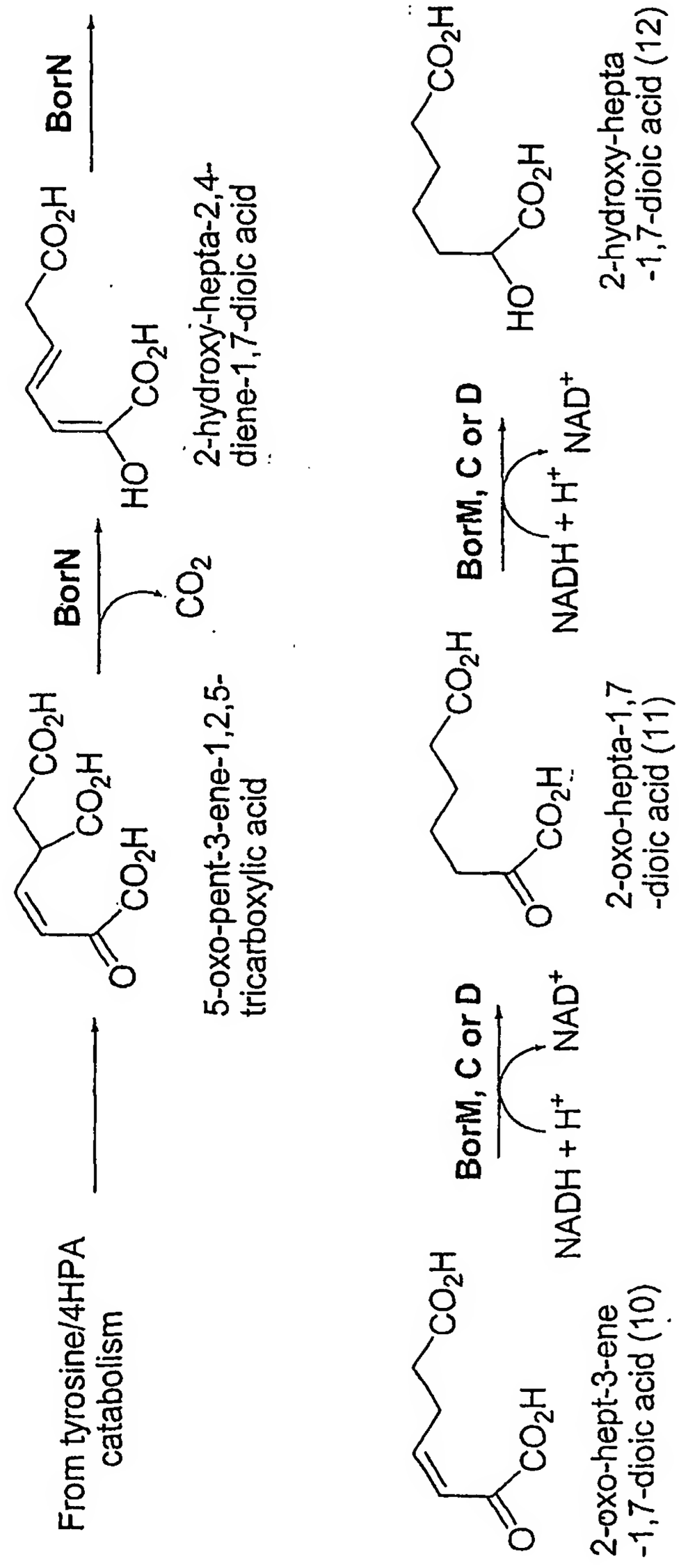

From tyrosine/4HPA catabolism
2-oxo-hept-3-ene -1,7-dioic acid (10)
NADH + H+ NAD+
BorE
trans-cyclopentane-1,2-dicarboxylic acid
BorM, C or D
NADH + H+ NAD+
2-oxo-hepta-1,7-dioic acid (11)
BorM, C or D
NADH + H+ NAD+
2-hydroxy-hepta -1,7-dioic acid (12)
activation of C2-hydroxyl?
2-OP-hepta-1,7-dioic acid (13) (P = H or activating group)
BorN
CO2
5-oxo-pent-3-ene-1,2,5-tricarboxylic acid
BorN
2-hydroxy-hepta-2,4-diene-1,7-dioic acid

Figure 4

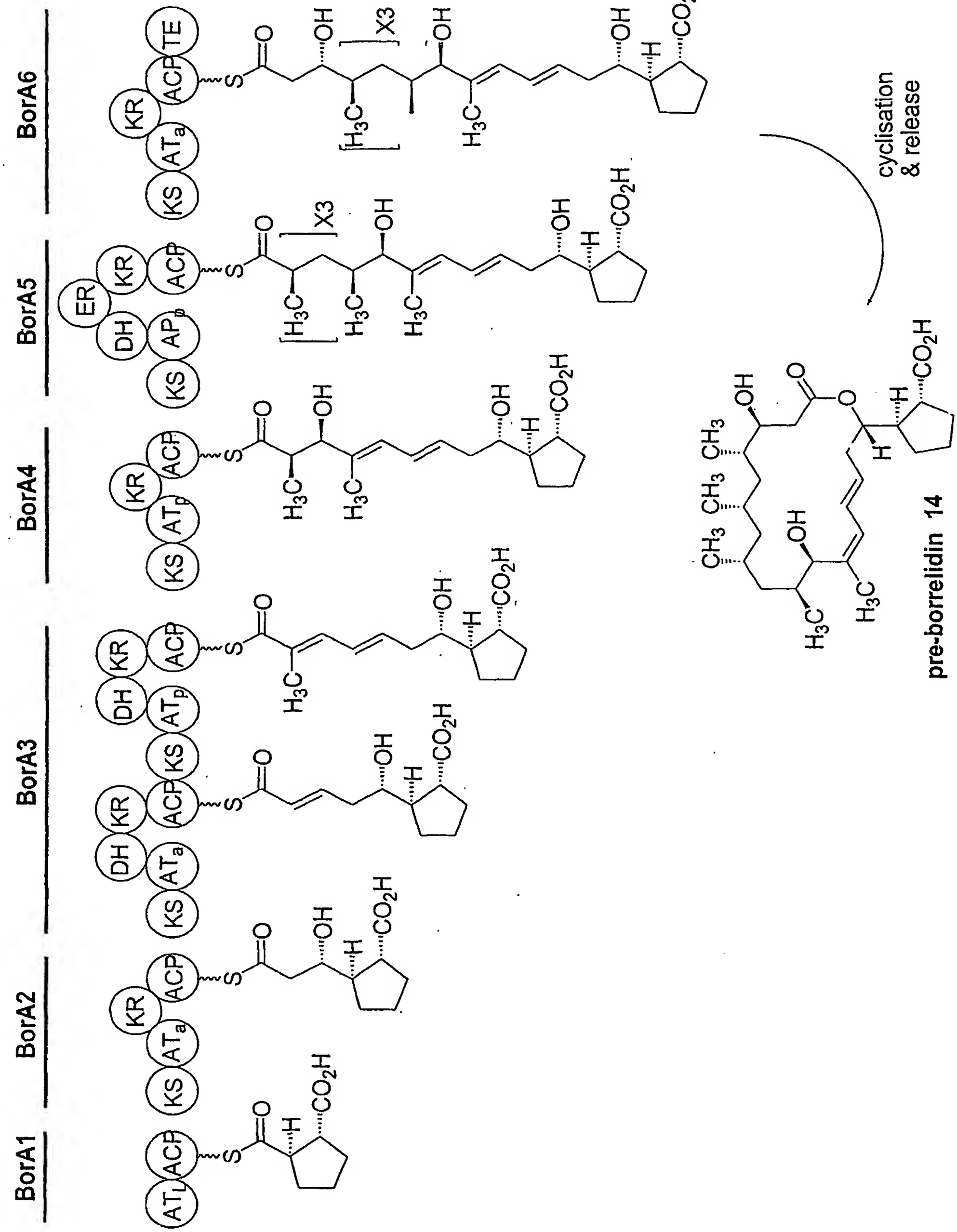

BorA6
BorA5
BorA4
BorA3
BorA2
BorA1
cyclisation & release
pre-borrelidin 14

Figure 5

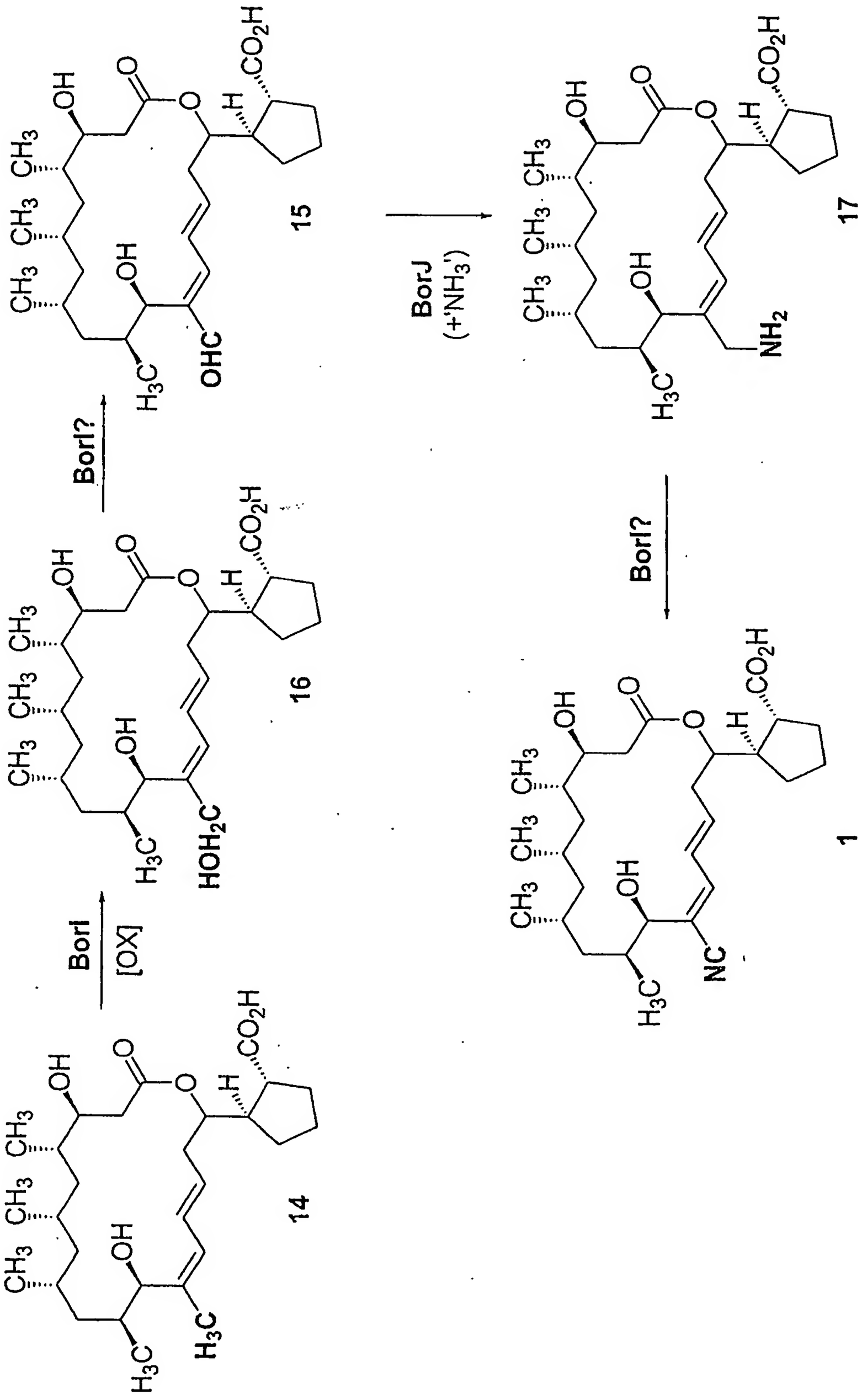
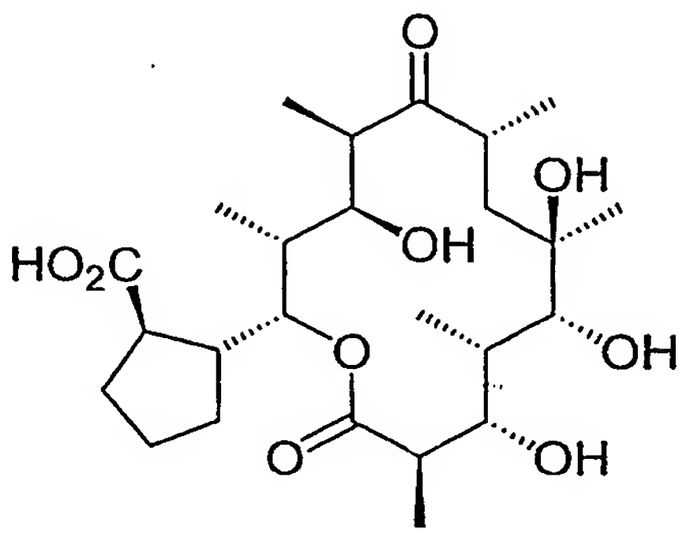

BorJ
(+'NH3')
BorI?
[OX]
BorI?
BorI?
15
16
17
1
14
OHC
HOH2C
NH2
NC
CO2H
OH
CH3
H3C
O
H

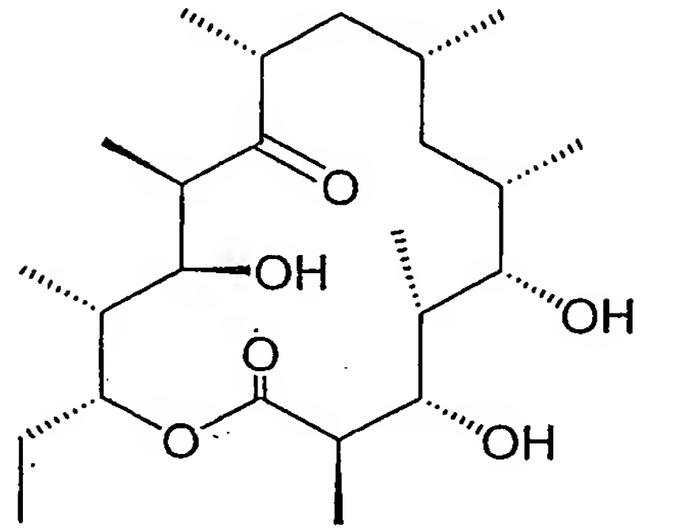
Figure 6

Figure 7

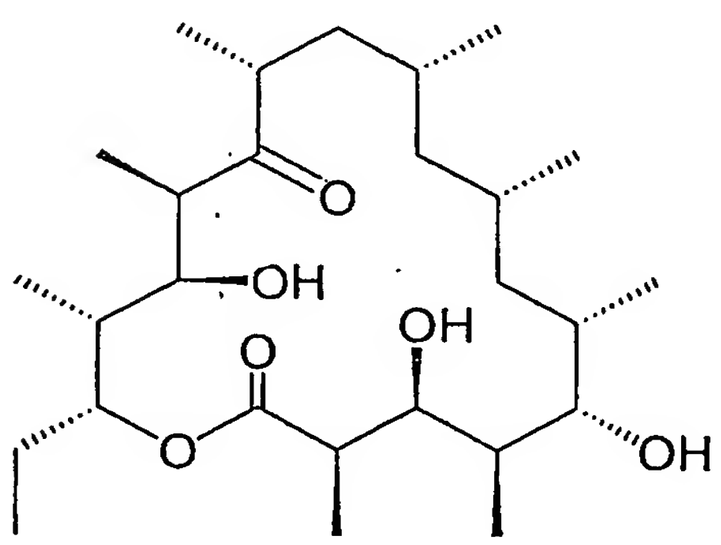


6

Figure 8



7



8

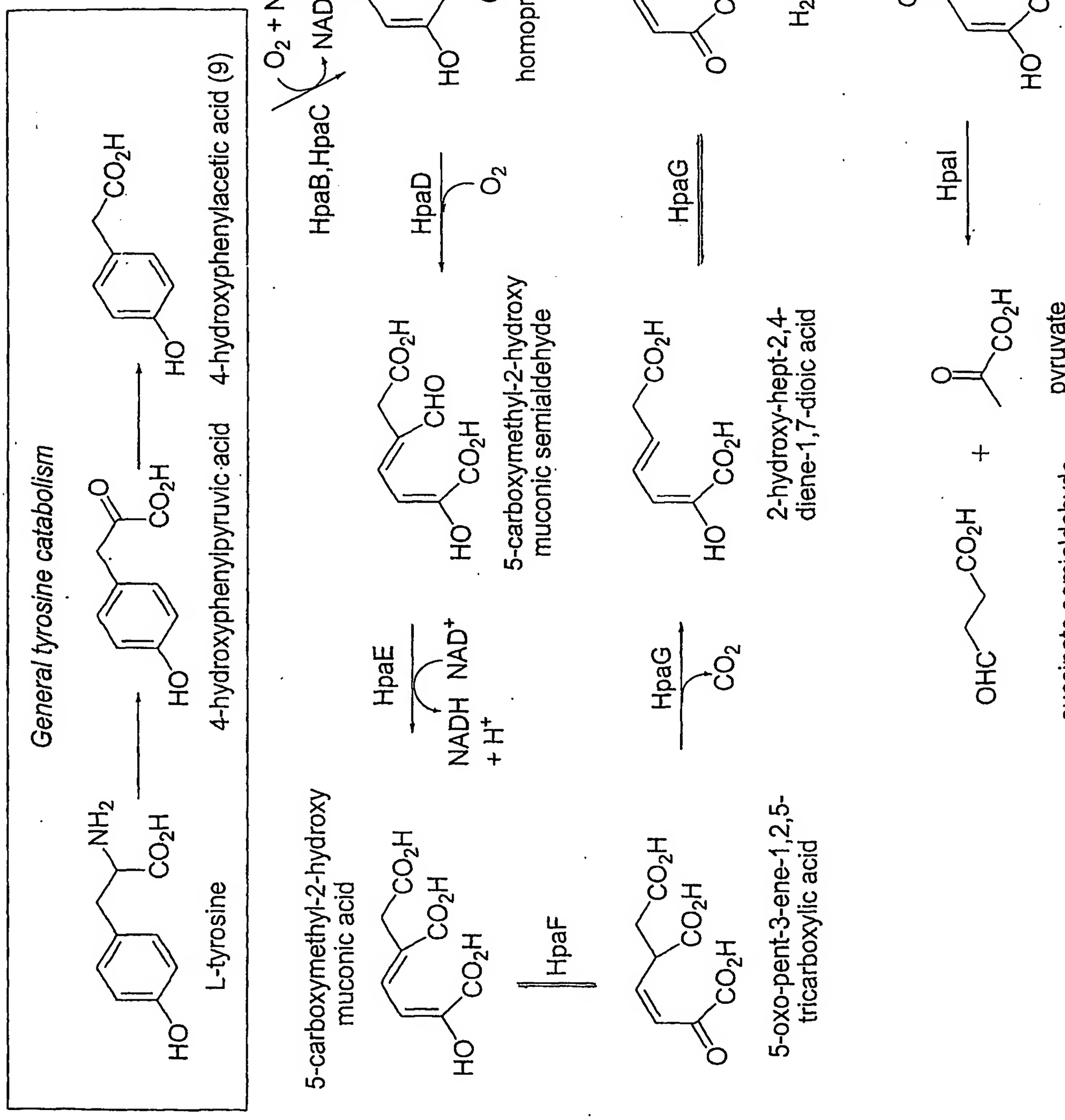
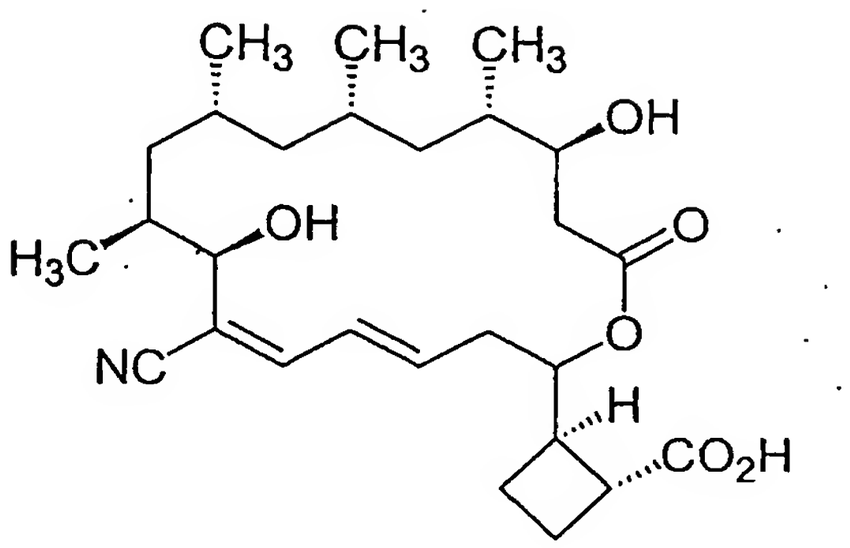
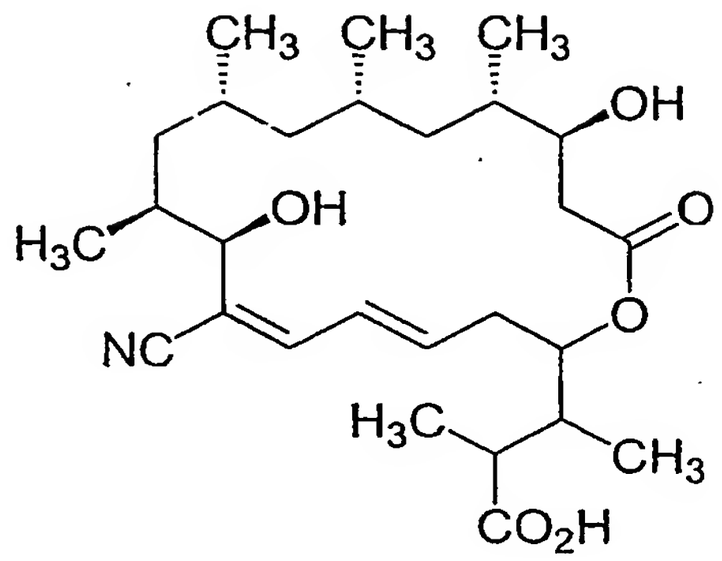

General tyrosine catabolism
L-tyrosine
4-hydroxyphenylpyruvic acid
4-hydroxyphenylacetic acid (9)
O_2 + NADH + H^+
NAD^+ + H_2O
HpaB,HpaC
homoprotocatechuic acid
2-oxo-hept-3-ene-1,7-dioic acid 10
H_2O
HpaH
2,4-dihydroxy-hept-2-ene-1,7-dioic acid
HpaE
NADH + H^+
NAD^+
5-carboxymethyl-2-hydroxy muconic semialdehyde
HpaD
O_2
HpaG
CO_2
2-hydroxy-hept-2,4-diene-1,7-dioic acid
HpaI
succinate semialdehyde
pyruvate
5-carboxymethyl-2-hydroxy muconic acid
HpaF
5-oxo-pent-3-ene-1,2,5-tricarboxylic acid

Figure 9

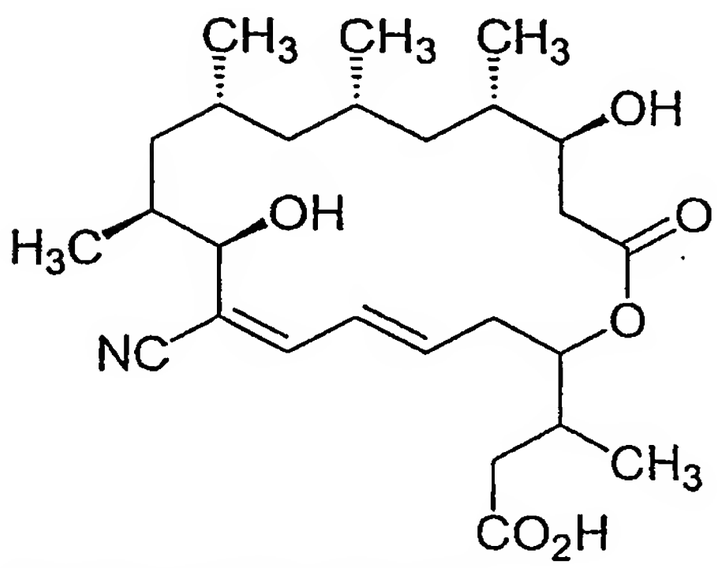
Figure 10



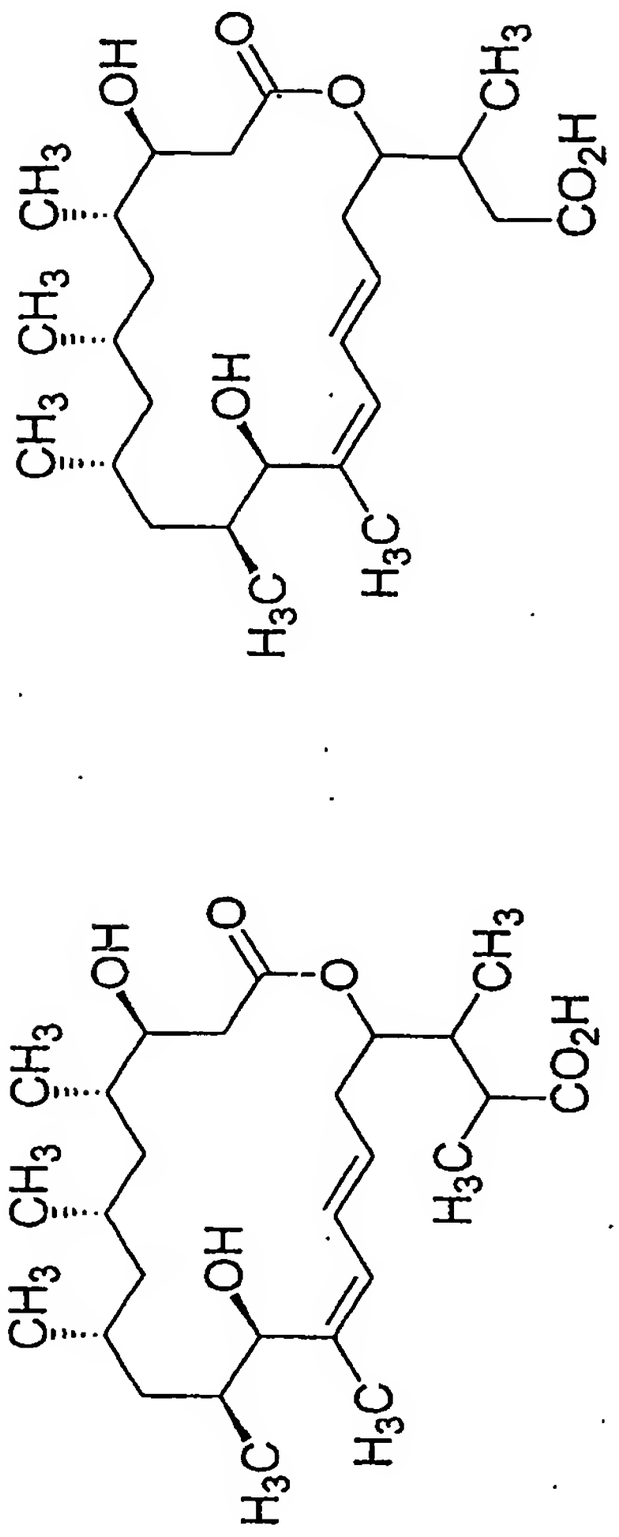
18: m/z = 474.3 ([M-H]$^-$)



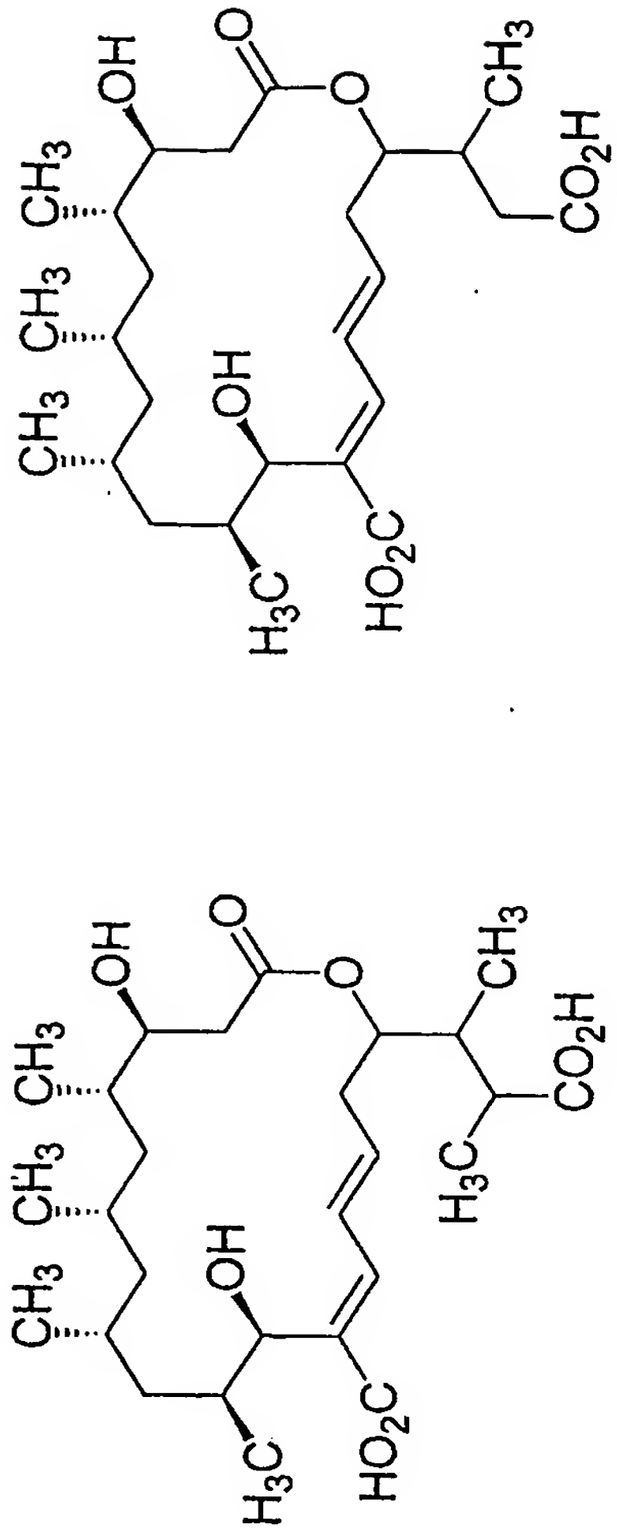
19: m/z = 476.3 ([M-H]$^-$)



20: m/z = 462.3 ([M-H]$^-$)



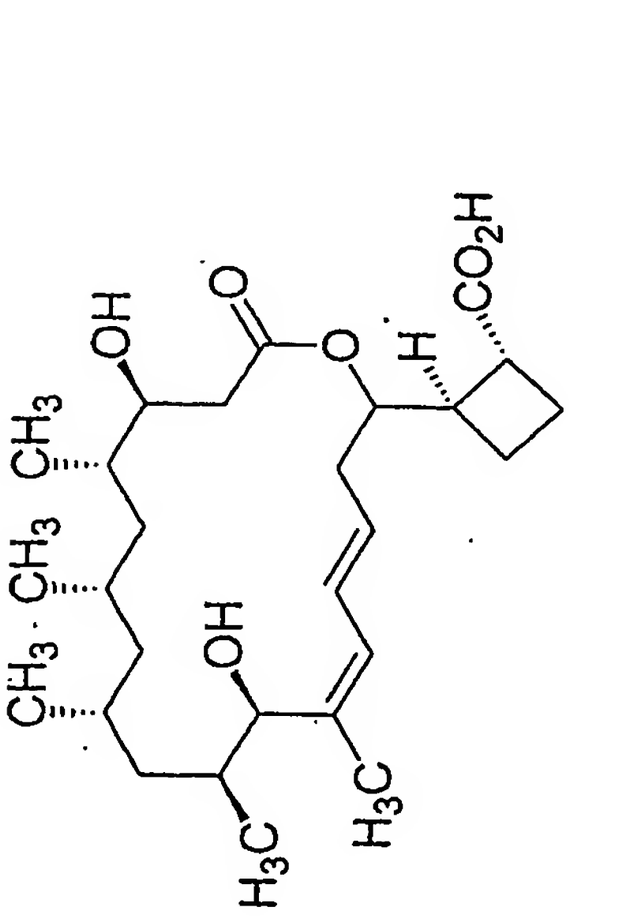
23: m/z = 451.3 ([M-H]$^-$)
λ_{max} = 240 nm



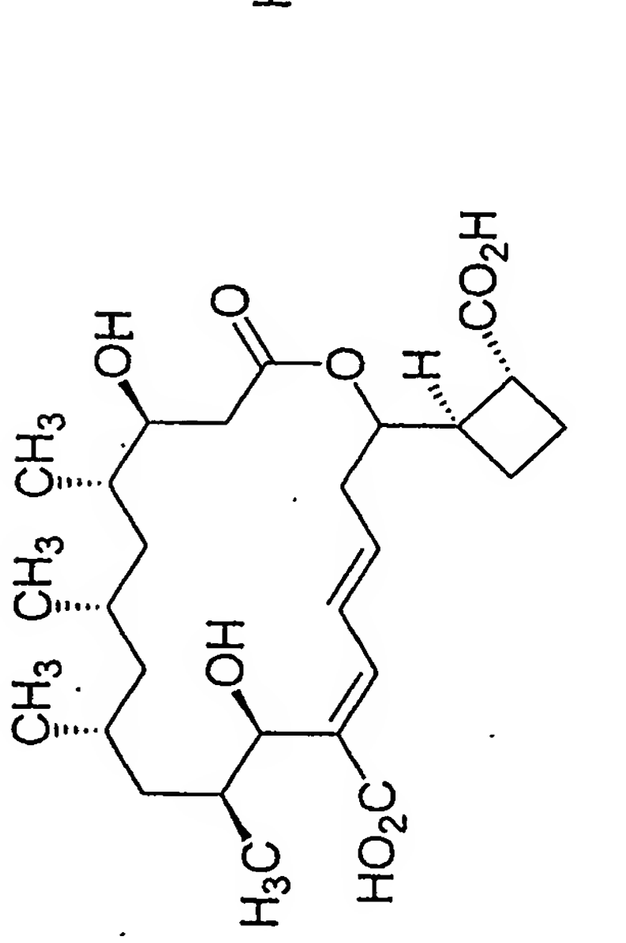
26: m/z = 481.3 ([M-H]$^-$)
λ_{max} = 262 nm

22: m/z = 465.4 ([M-H]$^-$)
λ_{max} = 240 nm

25: m/z = 495.3 ([M-H]$^-$)
λ_{max} = 262 nm



21: m/z = 463.3 ([M-H]$^-$)
λ_{max} = 240 nm



24: m/z = 493.3 ([M-H]$^-$)
λ_{max} = 262 nm

Figure 11